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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Flexible, Heat-Sealable Multilayer Film Made from Thermoplastic Elastomers with an Internal Barrier Layer

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Flexible, heat-sealable multilayer film made from  
thermoplastic elastomers with an internal barrier layer

A b s t r a c t

2123053

The present invention relates to heat-sealable, flexible multilayer films having at least three layers, with outer layers made of thermoplastic polyurethane and/or copolyetherester elastomers and an internal layer with liquid barrier properties made of ethylene/vinyl alcohol copolymers, wherein the thermoplastic elastomers used have a Shore D hardness of at least 35 and at most 72, both measured to DIN 53 505, and the ethylene/vinyl alcohol copolymers used have an ethylene content of 10-40 wt.% related to the total weight of the ethylene/vinyl alcohol copolymers.

WW 5379 - Foreign countries

2123053

Flexible, heat-sealable multilayer film made from thermoplastic elastomers with an internal barrier layer

The present invention relates to heat-sealable flexible  
5 multilayer films, the core layer and/or core layers of  
which are made from barrier polymers and the outer layers  
of which are made from thermoplastic elastomers. Due to its  
improved barrier properties towards organic liquids, in  
particular hydrocarbons and alcohols, the film is suitable  
10 for the production of low-loss storage or transport  
packages, in particular for fuels.

There are legal provisions relating to environmental  
protection which cover storage containers for liquid media  
15 hazardous to the environment. A known solution is to  
install the containers within bunds or to provide double-  
walled containers wherein the emphasis is upon protection  
of the soil and water courses from the stored media.

20 DE-GM 91 09 544 provides a comprehensive review of the  
embodiments of tank systems described in the relevant  
patent literature.

Most known structural measures to achieve the desired  
25 protective effect are suitable only for new tank storage  
due to the involved high technical efforts. Older fuel  
storage depots very often incorporate no safety measures  
complying with recent regulations. Since structural  
measures are often not practicable, protective systems with  
30 an internal film bag are used ('bag in box' system).

While protection of the soil and water courses, as laid  
down in *Bau- und Prüfgrundsätzen für den Gewässerschutz*  
[Principles of construction and testing for the protection  
35 of water courses], parts I and II, Institut für Bautechnik,  
Reichpietschufer 74-76, 10785 Berlin, Germany, is part of  
the present technical state of the art, there is now also

WW 5379 - Foreign countries

2123053

an increasing concern to prevent or minimise environmental damage caused by evaporating liquids, particularly those of organic kind.

5

Pouches made from flexible films or bags as well as internal liners installed within larger containers allow it to enclose stored liquids and prevent further evaporation of the liquid, which is otherwise possible by exchange of the vapour phase above the liquid. If the film constituting the bag is also sufficiently flexible, then the bag filled with the material being stored can accommodate to the volume of the stored liquid, as is for example described in German patent DE 40 00 427 A1, such that when filling and emptying the bag in the tank it is not necessary to expel the vapour phase which is at equilibrium with the stored material. In this case, it is only the surrounding air which does not contain any vapour of the stored liquid which is expelled when the volume of the bubble changes.

20

The use of plastic films for storing high-boiling organic liquids such as for example diesel fuel and/or for liners for storage containers for these substances has been known for a long time and is described in the relevant instructions, such as for example *Technische Regel für brennbare Flüssigkeiten* [technical rule relating to flammable liquids] n° 501 (TRbF 501 Richtlinie/Bau- und Prüfgrundsätze für Leckanzeigergeräte für Behälter [guideline/principles for the construction and testing of leakage indicators for containers]) edited by Verband der Technischen Überwachungsvereine e.V. (*Technische Regeln für brennbare Flüssigkeiten*, 1991, Carl Heymann Verlag, Luxemburger Straße 449, 50939 Cologne, Germany). TRbF 501 explicitly describes the construction principles for films made from plasticised polyvinyl chloride (PVC) for such applications. However, plasticised PVC's resistance

2123053

against many organic solvents and mineral oil products is not sufficient.

- Rubber-based elastomers as well have insufficient barrier
- 5 properties and, due to their crosslinked molecular structure, they do not offer the design-flexibility for easy adaption of bags to existing tank containers as thermoplastic film materials do.
- 10 In contrast, thermoplastic elastomers (TPE) are characterised by a combination of good mechanical properties, i.e. elevated tensile strength and tear propagation resistance, high extensibility, together with good flexibility at low temperatures and chemical
- 15 resistance. TPE have for a long time been known and consist of block copolymers. The different blocks or segments in their structure determine different properties of the TPE, usually a distinction is being made between hard and soft segments. The hard segment determines strength, while the
- 20 soft segment determines elasticity and flexibility. The different blocks of the hard and soft segments separate in the solid state which consequently exhibits a domain structure.
- 25 The combination of the different material properties strength and flexibility in one molecule is achieved by an alternating arrangement of different blocks. The so-called internal plasticisation means that elasticity or softness are inherent to the plastic and are unaffected by a change
- 30 in additive composition, as it occurs in the case of migration.

- The formation of physical networks by the combination of hard segments giving crystallites, glassy solidified
- 35 domains and/or by hydrogen bridge formation means that these networks are thermo-reversible, i.e. these materials

2123053

may be processed and shaped as thermoplastics and may also be heat-bonded.

- An review of the structure, production, properties and applications of TPE may be obtained from Hoffmann in *Kunststoffe* 80 (1990) 10, Legge in *Rubber Chemistry and Technology* 62 (1989) 529 and Goyert in *Swiss Plastics* 4 (1982) 7.
- 10 If explosive media are stored, there is an additional requirement for the films used to be antistatic in order to prevent any risk of ignition. In *Technische Regel für brennbare Flüssigkeiten* n° 401 (TRbF 401 *Richtlinie für Innenbeschichtungen von Behältern zur Lagerung brennbarer Flüssigkeiten der Gruppe A Gefahrenklasse I, II und der Gruppe B* [guideline relating to internal coatings for containers for the storage of flammable liquids of group A, hazard class I, II and of group B]) edited by Verband der Technischen Überwachungsvereine e.V. obtainable from Carl Heymans Verlag KG, Luxemburger Str. 449, 50939 Cologne, Germany, it is *inter alia* mentioned that coatings do not give rise to ignition hazards due to the formation of electrostatic charges if their resistance does not exceed  $10^8$  Ohm.
- 25 The hazards arising from a discharge of static electricity, together with possible preventive measures, are described in guideline n° 4 from *Berufsgenossenschaft der chemischen Industrie* [chemicals industry employer's liability insurance association] (ZH 1/200). It is explained there that for solid materials the formation of hazardous charges is not to be expected if their surface resistance is less than or equal to  $10^9$  Ohm, measured to DIN 53 482/VDE 0303, part 3 in a standard conditioning atmosphere at 23°C and 50% relative humidity.

2123053

The material properties of TPE may be modified, in a similar manner to those of standard plastics, with additives and fillers. Antistatic properties may successfully be imparted to plastics by the addition of  
5 carbon black, as explained by Hauf in *Materialwissenschaft und Werkstofftechnik* 23 (1992) 157 or Weßling in *Polymer Engineering and Science* 31 (1991) 1200.

Materials with surface resistances of  $> 10^{13}$  Ohm, measured  
10 to DIN 53 482, are generally described as insulators and those with resistances of  $< 10^5$  Ohm as conductors. Materials with a resistance between these limiting values are classified as static electricity dissipative or often simply as antistatic materials.

15 The use of antistatic coatings or outer layers is variously described in the relevant patent literature, for example DE-GM 18 22 483 describes completely synthetic woven fabrics sealed with polyester-urethanes, wherein a  
20 conductive coating is applied to only one side. In practice, coated woven fabrics have an undesirably large number of pinholes so that microleaks cannot be eliminated in such systems. Application of a conductive coating to only one side is inadequate.

25 DE 31 03 772 A1 describes multilayer film structures with conductive TPU outer layers. Plasticised PVC as the core material has inadequate barrier properties for diffusing fuel molecules. Even if more rigid grades of PVC are used,  
30 barrier properties may only be slightly improved and film flexibility is lost.

Coated or laminated woven fabrics are of a distinctly more heterogeneous nature than films, which nature is only  
35 unwillingly tolerated. Inherent to fabric layers is the risk of faster lateral diffusion, so that any possible material damage is accelerated.

2123053

The two-layer film structures described in JA 52-69486 have the disadvantage that only one of the two outer layers can be heat-sealed together.

- 5 Of particular importance is the lining of containers for the storage of materials with high vapour pressures, as they often occur with explosives, such as for example fuels. These substances frequently exhibit increased diffusion through the plastic materials used for container
- 10 linings. EP 0 461 836 A1 describes the necessity of an additional barrier layer in polyolefin materials when storing fuels and suggests the use of polyamides as barrier layer materials.
- 15 Polyamide is well known for its high strength and good chemical resistance. A comprehensive review of the properties, production and processing of this class of materials may be found in *Kunststoff-Handbuch*, vol. VI, Polyamides, Vieweg, Müller (eds.), Carl Hanser Verlag,
- 20 Munich 1966. However, using polyamides of a sufficient thickness to ensure satisfactory barrier properties leads to an undesirable reduction in flexibility.

Moreover, polyamide has barrier properties which are only

25 partially adequate for fuels, as explained by Leaversuch in *Modern Plastics International* 12 (1991) 14.

It is known from the relevant specialist literature, such as for example Rellmann & Schenck in *Kunststoffe* 82 (1992)

30 729, that barrier layer polymers such as ethylene/vinyl alcohol copolymers (EVAL) and saponified and/or partially saponified ethylene/vinyl acetate copolymers are used to reduce loss of stored media in rigid containers. However, the systems as for example described by Daubenbüchel in

35 *Kunststoffe* 82 (1992) 201 are not suitable for flexible storage containers due to their material structure.



2123053

The object of the invention was thus to provide a film which is capable of adapting to external shapes and is heat-sealable to itself, i.e. is weldable, such that flexible containers such as pouches, bags or internal  
5 liners for cans or tanks may be shaped from it. For safety reasons, these flexible containers should have a great abrasion and puncture resistance in order to forestall mechanical damage on repeated filling and emptying operations. This means the film should exhibit high tear  
10 strength and elongation at break, while also requiring only low stresses for a slight elongation.

The materials used should also be resistant to fuels, and films produced from them should moreover have good barrier  
15 properties towards the largest possible number of organic solvents.

It was also important to produce this film in such a way that it is heat-sealable or weldable to itself, while  
20 nonetheless being abrasion resistant and offering both thermal stability and elevated chemical resistance.

The required permeability, for example of unleaded premium petrol, should not exceed  $1 \text{ g}/(\text{m}^2 \text{ 24 h})$ , measured to  
25 DIN 53 532.

For the storage of oxidisable organic solvents with a high vapour pressure, i.e. explosive media, there is the additional object of achieving a sufficiently low surface  
30 resistance to exclude ignition hazards from discharges of static electricity. This resistance should be less than  $10^8$  Ohm, measured to DIN 53 482/VDE 0303, part 3, electrode arrangement A.

35 Barrier properties which are largely independent of environmental conditions should also be considered advantageous.

2123053

Despite the vigorous efforts of those skilled in the art, particularly plastic film manufacturers, to produce such a film, none has yet been made known to those experts interested in flexible barrier layer films.

5

It has now proved possible to achieve this object according to the invention with a heat-sealable, flexible multilayer film having at least three layers, comprising layers of different structural polymers which is characterised in  
10 that it has thermoplastic elastomers in the outer layers and an EVAL barrier layer as core and the layers are joined together by coextrusion and/or lamination.

Films suitable for the production of storage bags, pouches  
15 or liners which have at least three layers and are made from thermoplastic elastomers with an internal barrier layer of EVAL, preferably have a total thickness of 0.05 to 2 mm.

20 In addition to the stated minimum three layers, the film may contain further layers of other structural polymers which allow it to further improve the properties of the film according to the invention or to adapt it to the requirements of particular applications.

25

The sum of the thermoplastic elastomer outer layers has a content ranging from 20% to 98% related to the total weight of the film. Preferred films are those in which the sum of the outer layers is at least 30% and at most 80% related to  
30 the total weight of the film.

In a preferred embodiment, the film is of symmetrical structure such that it may be welded to itself without loss of properties and without regard to the layer structure.

35

Thermoplastic elastomers synthesised from hydrophilic raw materials are of particular interest as constituents for

2123053

the outer layers of films used in the storage of organic solvents and mineral oil products. Such elastomers are thermoplastic polyurethanes (TPU) and copolyetheresters (PEE), since they have lower affinity to hydrophobic  
5 mineral-oil based fuels.

It is not generally necessary to introduce reinforcing fabric into the film as the mechanical strength and stability of the film according to the invention is  
10 generally sufficiently high due to the use of tear-resistant materials, in particular the thermoplastic elastomers. By dispensing with such reinforcement, the film according to the invention gains chemical resistance as the penetration of possible damaging particles, which could be  
15 contained in the material being stored, is prevented.

At least one of the heat-sealable outer layers may if required be made antistatic. Suitable materials for imparting antistatic properties are conductive additives  
20 such as for example carbon blacks or intrinsically conductive polymers or metal particles. The conductive additives are incorporated into the molten TPE using the machines commonly used in the plastics industry such as kneaders or extruders, in particular double screw  
25 extruders.

When blending the electrically conductive additives, it proved successful to use processing auxiliaries which have a plasticising effect and very largely leave the polymer  
30 matrix after finishing the blending process, wherein no negative effects on properties remain. Such volatile processing auxiliaries are preferably compressed gases with an elevated plasticising action, carbon dioxide being particularly suitable for this purpose.

35 Carbon blacks with a BET surface area of greater than or equal to 600 m<sup>2</sup>/g (ASTM D-3037) and an average particle size

2123053

of less than 500 nm are preferably used as the antistatic additive. Carbon blacks fulfilling these requirements are commercially available, for example Printex XE 2 from Degussa or Ketjenblack EC 600 from Akzo. The preferred  
5 carbon black content to impart antistatic properties is suitably 5 to 20%.

Since the barrier properties of EVAL copolymers are very highly dependent upon their moisture content or the  
10 moisture content of their surroundings, it is advantageous not to use these copolymers as outer layers of films, but instead to incorporate them as core barrier layers in film structures.

15 It proved possible, as is known from food packaging film, to stabilise the barrier properties of the barrier layer to a very great extent independently of environmental moisture by introducing additional interlayers. Polyolefin materials proved particularly suitable for the production of such  
20 interlayers. Polyethylene polymers are used in a preferred embodiment.

The barrier properties of the film according to the invention against a commercial available, unleaded premium  
25 petrol are so pronounced that the permeability of this liquid is below 1 g/(m<sup>2</sup> 24 h).

The properties of the polymer raw materials used for the individual layers of the film according to the invention  
30 may be further improved with regard to the use according to the invention by the addition of suitable customary additives in effective quantities. Additives which may be used to this end include *inter alia* not only slip additives and lubricants but also colouring pigments, biocides and  
35 inorganic fillers or antiblocking agents, such as for example silica.

Preferred slip additives are not only carboxylic acid amides such as erucic acid amides, stearic acid amides and palmitic acid amides or polydiorganylsiloxanes, but also fluoroelastomers and inorganic slip additives such as molybdenum disulphide, but also stearic acid salts.

Suitable anti-blocking agents are for example organic polymers incompatible with the film matrix or inorganic substances such as silicates, silicon dioxide and calcium carbonate. Inorganic substances such as silicon dioxide with an average particle size of 1 to 10  $\mu\text{m}$  have proved particularly successful anti-blocking agents. The effective quantity of these anti-blocking agents to be added is 0.5 to 6 wt.%, preferably 2 to 4 wt.% related to average film weight.

Surprisingly, when imparting electrically conductive properties to the outer layers of the film according to the invention, wherein the described carbon black is preferably used, its particles having a spacing effect, it was found that the quantity of further anti-blocking agents added could be reduced by the extent to which electrically conductive additives were included in the formulation and/or could be completely omitted.

A comprehensive description of usual additives and their mode of action may be referred to in Gächter & Müller, *Taschenbuch der Kunststoffadditive* [handbook of plastics additives], Carl Hanser Verlag, Munich 1989.

In order to ensure the long term stability of the properties of the film according to the invention, it may contain suitable additions of stabilisers in effective quantities, preferably hydrolysis stabilisers and/or photostabilisers and/or antioxidants.

2123053

Light-absorbing substances are suitable to achieve photostabilisation, benzoates and/or phenylsalicylates which absorb high-energy UV light being in particular used, but also substituted acylates and benzotriazoles. Quenchers may  
5 also be used for photostabilisation, preferably nickel-organyl chelates and/or nickel dithiocarbamates.

Preferably used hydrolysis stabilisers are carbodiimides, in particular non-migrating variants as polycarbodiimides,  
10 but also hydroxyethyl ureas.

Suitable antioxidants for use in the film according to the invention are both so-called primary antioxidants, secondary phosphites or phosphonites sterically hindered by  
15 substitution at the oxygen and/or sterically hindered phenols and also mixtures of primary and secondary antioxidants.

Stabiliser systems suitable for use in the plastics used in  
20 the film according to the invention are, for example, described by Rek and Bravar in *J.Elast.Plast* 12 (1980) 245.

The substances to be added may be incorporated by direct mixing during polymer production or also by the addition of  
25 a masterbatch or a liquid or polymer concentrate containing the additives, in an amount corresponding to the desired quantity to be incorporated.

All the polymer materials used for the film according to  
30 the invention may be processed in customary plastics processing machinery, such as for example extruders. Generally used tools, such as flat film dies with downstream chill rolls or downstream coating units, but also blown film dies combined with appropriate collapsing  
35 arrangements, may be used to form the films.

2123053

- Purpose-designed tools, for example coextrusion dies, may be used to join the layers. If it is impossible to use a single tool directly to process two different materials which are necessarily used in the film according to the invention due to very different processing behaviour, the layers may also subsequently be bonded by thermal lamination, for example by flame lamination, by lamination using a suitable adhesive system or also by any other customary lamination process.
- 10 In a preferred embodiment, polyurethane adhesives are used to laminate differing film webs, wherein adhesive systems are used which exhibit strong molecular crosslinking, such that they are only slightly swollen but not dissolved by migrating molecules of the stored substances.
- 15 Interlayer adhesion may, if necessary, be distinctly improved by the use of bonding resins.
- 20 There is a great variety of commercially available grades of bonding resins. These are generally copolymers with at least two comonomers, but multipolymers with up to more than five different comonomers are also used.
- 25 A preferred comonomer in the bonding resins is in particular ethylene, which improves adhesion with non-polar polymers. Maleic anhydride is also preferably incorporated into bonding resins. Due to the anhydride functional group, this substance renders a strong bond with polar, particularly protic groups possible. Comonomers containing vinyl acetates, acrylates, methacrylates and butyl acrylates as the acid group are also widely used, since they have a bonding effect due to their polar organic molecular structure, wherein butyl acrylates are preferred comonomers.
- 30  
35

2123053

When using bonding resins containing maleic anhydride, adhesion of the structure is often found to improve with storage time of the film, a phenomenon brought about by molecular transformations which are initiated during processing, but which, due to their slow progress, only later achieve the desired level of bonding strength.

The surface properties of the film according to the invention may be modified on one or both sides. Suitable treatments are in particular corona, plasma or fluorine treatments. Use of these latter treatments means that the barrier properties of the film according to the invention may be optimally adapted to the expected contact medium or further improved.

Such surface-treatment processes for plastic films are comprehensively described by Dorn & Wahono in *Maschinenmarkt* 96 (1990) 34-39 or Milker & Möller in *Kunststoffe* 82 (1992) 978-981.

The invention is illustrated in greater detail below with examples and comparative examples.

**Example 1**

A symmetrical film was coextruded using a three-layer die. The surface layers were made from a TPU with a poly(oxytetramethylene)diol soft segment prepared from tetrahydrofuran and a hard segment with a Shore A hardness of 86 prepared from 4,4'-diisocyanatodiphenyl-methane (MDI) and butanediol, the core layer was made from ethylene-vinyl alcohol copolymer (EVAL). The EVAL used had an ethylene content of 38 wt.% related to the total weight of the EVAL used. At this ethylene content, the EVAL has only slight barrier action, but it may be directly processed together with the TPU due to their similar processing temperatures.



2123053

The outer layers of the blown film were each of an average thickness of 90  $\mu\text{m}$  and the core layer of an average thickness of 20  $\mu\text{m}$ .

5 Example 2

A TPU was blended with 10% of an elevated surface area carbon black, Ketjenblack EC 600 in order to obtain conductive properties. The TPU, which had a soft segment prepared from adipic acid and hexa-methylenediol and a hard segment prepared from MDI and butanediol, had a Shore A hardness of 93 or a Shore D hardness of 47. It was necessary to use amide waxes to incorporate the carbon black. The conductive TPU was coextruded with a bonding resin and an EVAL using a three-layer die to produce an asymmetrical structure.

The ethylene content of the EVAL was 32 wt.% related to the total weight of EVAL. The bonding resin used was a copolymer of ethylene, butyl acrylate and maleic anhydride. The ethylene content was provided by an LLDPE.

The TPU layer was 90  $\mu\text{m}$  thick, the bonding resin and EVAL layers were each 10  $\mu\text{m}$  thick.

In a further processing stage, the surfaces of the EVAL layers were melted using an infra-red radiant heater and, by bringing two webs together, joined into a symmetrical film with an EVAL core layer surrounded by bonding resin layers and TPU outer layers.

Example 3

A plasticised PEE raw material of Shore D hardness 60, consisting of hard segments prepared from terephthalic acid and ethylene glycol and soft segments of poly(oxytetramethylene)diol, was compounded in a kneader with a

2123053

proportion of 8 wt.% of conductive carbon black, Ketjenblack EC 600, in relation to the total weight of compound obtained. No plasticising auxiliaries capable of migrating to the film surface were used during compounding.

- 5 A single layer blown film was extruded from this compound. The same was done to prepare a film from an EVAL with an ethylene content of 29 wt.% related to the total weight of EVAL used. The PEE and EVAL had processing temperatures which were more than 30°C apart, so that they could not be  
10 processed in a single die. The barrier structure was obtained by adhesive lamination of the PEE films on both sides of the EVAL film. A crosslinking polyurethane adhesive dissolved in an organic, polar, aprotic solvent was applied and the films bonded together under the action  
15 of pressure and heat using conventional laminating equipment.

The average thickness of the conductive PEE films was 100 µm, that of the EVAL film 15 µm.

20

**Example 4**

- A conductive polyurethane, produced in the same manner as in example 2, was converted into a two-layer TPU film in a  
25 blown film coextrusion die together with another TPU, the soft segment of which was prepared from adipic acid and hexamethylenediol, and the hard segment from MDI and butanediol, of Shore A hardness 96 or Shore D hardness 54, the layers of which film were each 50 µm thick.

30

- A coextruded three-layer film produced from polyamide 6 and EVAL, with outer layers of polyamide and a core layer of EVAL, was used as the barrier film. This symmetrical barrier film was 15µm in thickness, wherein the thickness  
35 of the EVAL layer was 2 µm and that of the polyamide layers enclosing it 6.5 µm each.

## 2123053

Films according to the invention of thickness 220  $\mu\text{m}$  were produced using a crosslinking polyurethane adhesive, wherein the two-layer TPU films described above were laminated on both side of the barrier film. Lamination was performed such that the layers rendered conductive with carbon black were on the outside of the finished laminated film structure.

### Example 5

10 A film was produced in a three-layer blown film coextrusion die with a core of a bonding resin of 10 $\mu\text{m}$  in thickness. One of the outer layers, each of which were 50  $\mu\text{m}$  thick, consisted of a conductive TPU, the soft segment of which  
15 was prepared from adipic acid and hexamethylenediol and the hard segment from MDI and butanediol. The Shore A hardness of the TPU was 93, or the Shore D hardness 47. The other outer layer, also 50  $\mu\text{m}$  thick, consisted of a linear low density polyethylene of density 0.935 g/cm<sup>3</sup> and an MFI of  
20 0.5, measured at 190°C with a test weight of 2.16 kg.

A coextruded, symmetrical three-layer film produced from polyamide 6 and EVAL was used as the barrier layer with outer layers of polyamide and a core layer of EVAL (c.f.  
25 example 4). This barrier film was 80  $\mu\text{m}$  thick, wherein the thickness of the EVAL layer was 6  $\mu\text{m}$  and that of each of the polyamide layers enclosing it 37  $\mu\text{m}$ .

Films according to the invention were obtained by using a  
30 crosslinking polyurethane adhesive, wherein the first stated three-layer films were laminated on both sides of the barrier film. Adhesive lamination of the first stated three-layer films onto the barrier film was performed on the non-conductive layers of low density polyethylene, such  
35 that the outer layers of the finished laminated film structure consisted of carbon black filled TPU layers.

Comparative example 1

2123053

A film was melt-processed from a commercially available thermoplastic polyurethane with an elastic ether segment by  
5 extrusion and subsequent casting onto a chill roll. The TPU had a poly(oxytetramethylene)diol soft segment prepared from tetrahydrofuran, together with a hard segment prepared from MDI and butanediol. The polyurethane used had a Shore A hardness of 85. 2% silicon dioxide and 0.4% amide wax,  
10 each related to the total quantity of film, were added as processing auxiliaries. The thickness of the film described was 400 µm.

Comparative example 2

15 An elevated surface area, electrically conductive carbon black, Ketjenblack EC 600, was incorporated into a TPU of Shore A hardness 93 or Shore D hardness 47 using a kneader. The TPU was characterised by a soft segment prepared from  
20 adipic acid and hexamethylenediol and a hard segment prepared from MDI and butanediol. The polymer was carefully plasticised by adding amide waxes. A blown film of 200 µm in thickness was obtained by extrusion.

25 Comparative example 3

A calendered film produced from plasticised PVC was used as a further comparative example. Flexibilisation was achieved by the addition of 20 wt.% dioctyl phthalate related to the  
30 total weight of the film. The thickness of this comparative film was 300 µm.

Comparative example 4

35 A PEE raw material of Shore D hardness 60 consisting of hard segments prepared from terephthalic acid and tetramethylene glycol and soft segments of poly(oxytetra-

2123053

methylene)diol was melted in an extruder. A film was produced from the melt using a blown film die. After collapsing, edge-trimming and separation, the film so obtained had a thickness of 200  $\mu\text{m}$ .

2123053

Table

Table 1	Petrol permeability g/(m <sup>2</sup> 24 h)	Electrical surface resistance Ohm	Tear strength N/mm <sup>2</sup>	Elongation at break %	Softening point °C
Example 1	0.2	$3 \cdot 10^{12}$	55.2	360	143
Example 2	< 0.1	$6 \cdot 10^5$	51.1	550	135
Example 3	< 0.1	$7 \cdot 10^6$	27.6	480	157
Example 4	0.2	$6 \cdot 10^5$	29.2	590	135
Example 5	0.1	$5 \cdot 10^5$	23.1	690	148
Comparative example 1	10.4	$3 \cdot 10^{12}$	72.0	480	140
Comparative example 2	16.3	$6 \cdot 10^5$	39.1	440	174
Comparative example 3	33.8	$6 \cdot 10^4$	12.5	170	74
Comparative example 4	7.6	$5 \cdot 10^{12}$	36.1	645	157

As may clearly be seen from a comparison of the examples and the comparative examples, the films according to the invention are superior to the comparative films in terms of the desired properties.

#### Determination of petrol permeability

The petrol permeability of the films is determined according to DIN 53 532 "Determination of liquid permeability of elastomer films". Pursuant to DIN 50 014, determination was performed at a temperature of 23°C in ambient air with a relative humidity of 50% (standard conditioning atmosphere 23/50). The petrol used was a customary commercial unleaded premium petrol according to DIN 51 607/EN 228.

2123053

Measurement of surface resistance

- Electrical surface resistance is measured according to DIN 53 482/VDE 0303, part 3, in standard conditioning atmosphere 23/50. Electrode arrangement A consisting of two sprung parallel electrodes 100 mm in length and 10 mm apart was used.

Measurement of tear strength and elongation at break

- 10 Tear strength and elongation at break are determined according to DIN 53 455. Standard conditioning atmosphere 23/50 is used. Test strips with a clamping distance of 50 mm must be used.

15 Determination of softening range

- Softening range is determined on a Kofler hot plate. To this end, a strip of film of dimensions 30 x 200 mm is laid upon the previously calibrated Kofler heating bench. Starting from a low temperature, the film strip is lifted up after a waiting period of 30 seconds. The temperature range at which the film adheres to the Kofler heating bench gives the softening range.

2123053

Patent claims

1. Heat-sealable, flexible multilayer films having at least three layers, with outer layers made of thermoplastic polyurethane and/or copolyetherester elastomers and an internal layer with liquid barrier properties made of ethylene/vinyl alcohol copolymers, characterised in that the thermoplastic elastomers used have a Shore D hardness of at least 35 and at most 72, both measured to DIN 53 505 and the ethylene/vinyl alcohol copolymers used have an ethylene content of 10-40 wt.% related to the total weight of the ethylene/vinyl alcohol copolymers.
2. Multilayer film according to claim 1, characterized in that, between the outer layer of thermoplastic elastomers and the barrier layer of ethylene/vinyl-alcohol copolymers, the film contains at least one additional layer of at least one further polymer which may be processed as a thermoplastic, preferably polyamides and/or polyolefins.
3. Multilayer film according to claims 1 and/or 2, characterized in that, reactive adhesive systems, preferably polyurethane adhesives, or bonding resins are used to improve or achieve adhesion of the structure.
4. Multilayer film according to one of claims 1 to 3, characterised in that the film is of a symmetrical structure in terms of the position of the individual layers in relation to the geometric centre of the film.



2123053

5. Multilayer film according to one of claims 1 to 4,  
characterised in that at least one of the thermo-  
plastic elastomer outer layers contains conductive  
additives, such that its electrical surface resistance  
5 is at most  $10^9$  Ohm, measured to DIN 53 482, electrode  
arrangement A.
6. Film according to one of claims 1 to 5, characterised  
in that its total thickness is from 50 to 2000  $\mu\text{m}$ ,  
10 preferably from 200 to 800  $\mu\text{m}$ .
7. Film according to one of claims 1 to 6, characterised  
in that the sum of the thicknesses of the outer layers  
constitutes a proportion of 20% to 98%, preferably 30%  
15 to 80% of the total layer thickness of the film.
8. Use of the multilayer film according to one of claims  
1 to 7, characterised in that the film is used to  
produce flexible containers and/or flexible bags for  
20 lining dimensionally stable containers.
9. Use of the multilayer film according to claim 8,  
characterised in that the film is used as an  
additional cover and vapour barrier for the storage of  
25 flammable liquids.
10. Use of a film according to claim 8 and 9,  
characterised in that the film is used to produce  
covers for the storage of petrol fuels.

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